Preparation and characterization of simulated fuel debris specific to the Fukushima accident

M. Takano, T. Nishi, A. Onozawa

Japan Atomic Energy Agency, Nuclear Science & Engineering Center, Tokai, Ibaraki 319-1195, Japan
takano.masahide@jaea.go.jp

1. Background and objectives

- Investigation of characteristic data of fuel debris for its removal operation and appropriate management
- Factors affecting debris characteristics specific to the Fukushima accident
  - Seawater injection, no reflood : salt deposit on high temp. corium
  - B_4C control blade : chemical form of boron in solidified core melt?
  - MOX fuel, FPs
  - Large amount of MCCI products at the bottom of containment vessel
- Lab-scale experiments on simulated debris to understand the above factors

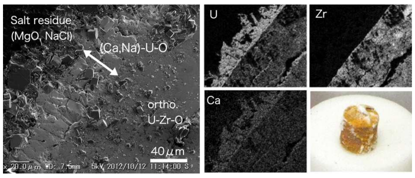
2. High temperature reaction between $(U,Zr)O_2$ and sea salt deposit

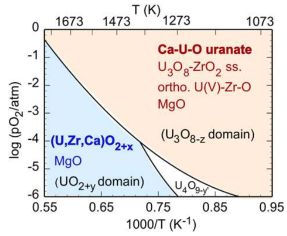
- Simulated corium: $(U_{0.4}Zr_{0.6})O_2$ (metastable fcc), $(U_{0.15}Zr_{0.85})O_2$ (tet.+mon.)
- Salt powder prepared from natural seawater:
  NaCl / $MgCl_2{\cdot}6H_2O$ / $MgSO_4{\cdot}H_2O$ / $CaSO_4$ / KCl = 87.8/5.8/2.9/1.8/1.7 (mol%)
- Isothermal treatment and analyses (XRD and SEM/EDX)
  Powder mixture / corium pellet in salt bed
  815 ~ 1395 °C, 2 ~ 20 h, under Ar or air flow

- Thermal decomposition of salt components
  Vaporization of NaCl above Mp. (800 °C~)
  Stable, crystalline MgO from chloride and sulphate
  CaO (?) from sulphate, most reactive with corium
  Evolution of HCl (corrosive) and SOx (oxidizing) gases

- Reaction products depends on oxygen partial pressure (pO_2)
  Under high pO_2 where U_3O_{8-z} is stable:
  - Dense Ca(+Na)-U-O uranate layer on the corium surface
  - $(U,Zr)O_2$ oxidized to orthorhombic U(V)-Zr-O and U_3O_8-ZrO_2 ss.

  Under low pO_2 where UO_{2+x} is stable:
  - $(U,Zr,Ca)O_{2\pm x}$ solid solution on the corium surface
  - But low diffusivity of CaO



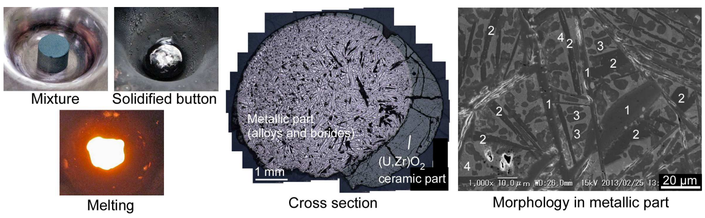


(Left) Cross sectional SEM image of sea salt/$(U_{0.4}Zr_{0.6})O_2$ reaction product. The pellet surface is covered by the typical orange-coloured uranate layer. (Air atmosphere, 1002 °C, 12 h)
(Right) Stable reaction products shown on the UO_2-U_3O_8-U_4O_9 boundary diagram.

3. Characterization of solidified core melt involving B_4C control blade

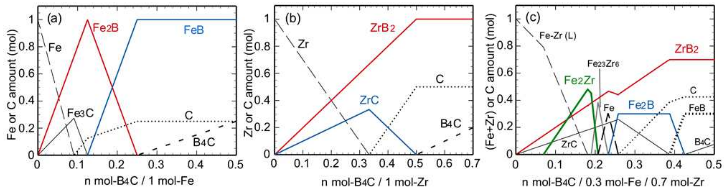
3.1. Phase identification in arc-melted specimens

- Investigating the phase relationships in the solidified core melt (ex. molten pool)
- Fuel materials: $(U,Zr)O_2$, Zr   Control Blade materials: B_4C, SS316L
- Arc melting of compacted mixtures under Ar atmosphere, subsequent annealing under Ar or Ar-0.1%O_2 atmosphere
- Phase identification on the cross section by XRD and SEM/EDX



Example of the arc-melted mixture of B_4C/SS/Zr/$(U,Zr)O_2$. The melt is solidified into $(U,Zr)O_2$ ceramic part and metallic part. The phases marked with numerals are ZrB_2 (1), $(Fe,Cr,Ni)_2B$ (2), Fe-Cr-Ni alloy (3), and $(Fe,Cr,Ni)_2(Zr,U)$ intermetallic (4).

- Experimental results verified qualitatively by thermodynamic assessment on a simplified B_4C–Fe–Zr system
- Phase relationships in the metallic part dominated by the initial B_4C/Zr ratio



Thermodynamic calculation of equilibrium compounds in B_4C/Fe (a), B_4C/Zr (b), and B_4C/Fe/Zr (c) systems at 1400 °C. In the actual cases of SS, Fe-Cr-Ni + $(Fe,Cr,Ni)_2(Zr,U)$ region expands considerably instead of Fe_2Zr + Fe in (c).

	Large <—— *B_4C/Zr ratio* ——> *Small*
Ceramic part	$(U,Zr)O_2$
Metallic part (alloys, borides, and carbide)	$(Fe,Cr,Ni)_2(Zr,U)$ + Fe-Cr-Ni buffer alloy ZrB_2 $(Fe,Cr,Ni)_2B$ — — — ZrC

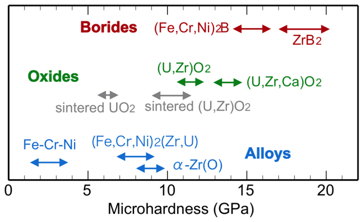
Schematic of the phase relationships in the solidified BWR core melt as a function of the initial B_4C/Zr ratio, under low oxygen partial pressures.

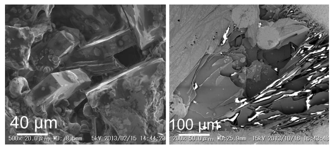
3.2. High temp. oxidation behaviour

- Annealing of a piece at 1500 °C for 10 h under $pO_2=1\times10^{-3}$ atm (≈ steam cond.)
- Metallic part remelted during the isothermal treatment
- Zr and U in the alloy, Zr in ZrB_2 selectively oxidized : $(Zr,U)O_{2+x}$ scale formed on the surface, instead the $(Fe,Cr,Ni)_2B$ matrix extensively formed inside
- No ferrous oxides formed under this condition

3.3. Microhardness of phases in solidified core melt

- A basic mechanical property for considering machining tools for debris removal
- Employed a micro Vickers tester
- Borides, especially ZrB_2, are considerably harder than any other materials : potentially barrier for cutting tools

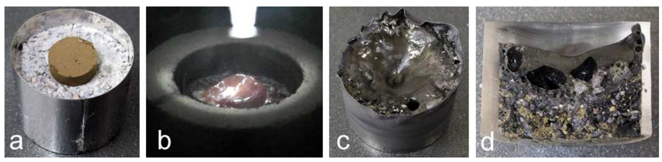




(Left) Microhardness ranges for the various phases in solidified specimens.
(Right) SEM images of crystalline ZrB_2 exposed in voids with different forms.

4. Other research works ongoing

- Phase relationships in U-Zr-O system under oxidizing condition (U_3O_{8-z} domain)
- Phase relationships in simulated MCCI product : arc melting (homogeneous melt) or light-concentrating heating (temp. gradient) of concrete/SS/Zr/$(U,Zr)O_2$ system
- Bulk mechanical properties for machining tools : compressive strength, Young's modulus, fracture toughness, etc.
- Chemical behaviour of debris in water (boric acid, hydrogen peroxide, etc.)
- Development of debris dissolution technique for destructive chemical analysis
- Effective use of TMI-2 debris specimens for verification



Example of the preparation of simulated MCCI product. SS/Zr/$(U,Zr)O_2$ mixture on a concrete piece (a), melting by light-concentrating heating (b), solidified state (c), cross section (d).

5. Conclusions and Acknowledgements

- Various types of simulated fuel debris specific to the Fukushima accident were prepared and characterized to contribute for the removal operation and management.
- Among the sea salt components, CaO decomposed from sulphate was found to be most reactive with $(U,Zr)O_2$ corium. The reaction products depends on the oxygen partial pressure, in other words, the oxidation state of uranium.
- The phase relationships in the BWR-type core melt were investigated. ZrB_2 and ferrous borides potentially form in the alloy matrix of Fe-Cr-Ni and $(Fe,Cr,Ni)_2(Zr,U)$. These borides are extremely hard materials.
- This paper includes the results of research program funded by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI) of Japan.

References: M. Takano et al., "High temperature reaction between sea salt deposit and $(U,Zr)O_2$ simulated corium debris", J. Nucl. Mater. 443 (2013) 32-39.
M. Takano et al., "Characterization of solidified melt among materials of UO_2 fuel and B_4C control blade", J. Nucl. Sci. Technol. 51 (2014) 859-875.

Poster ID Number: IAEA-CN-235-86
IEM on Strengthening Research and Development Effectiveness in the Light of the Accident at the Fukushima Daiichi Nuclear Power Plant,
IAEA Headquarters, Vienna, Austria, 16–20 February 2015